Improving the measurement of the Modified Fouling Index using nanofiltration membranes (NF–MFI)

Sarah Khirani*, Roger Ben Aim, Marie-Hélène Manero
INSA de Toulouse, 135, avenue de Rangueil, 31077 Toulouse Cedex 04, France
Tel. +33 (5) 61 55 97 56 Fax: +33 (5) 61 55 97 60; email: sarah.khirani@insa-toulouse.fr

Abstract

Fouling is the major issue when using membranes for water treatment. Several parameters have been proposed for measuring a fouling potential and using it as a predictive tool for assessing the adequacy of pre-treatment. Up to now, the Silt Density Index and the $MFI_{0.45}$ (Modified Fouling Index) are used, but they do not reflect the real potential of fouling. In fact, particles smaller than 0.45 µm responsible for fouling are not taken into consideration. An improvement of the determination of the fouling index is proposed by using NF membranes and strictly defined working conditions (constant transmembrane pressure).

Keywords: Fouling index; Modified Fouling Index; Nanofiltration; Transmembrane pressure

1. Introduction

When using NF or RO membranes, a fast and accurate measurement of the fouling potential of the feed water is needed. The Silt Density Index and Fouling Index (FI) are presently the only standard methods, but their limitations have been evidenced by several studies [1,2]. More recently, other methods have been developed like the Modified Fouling Index (MFI) and the Mini-Plugging Factor Index [3].

As the $MFI_{0.45}$ developed by Schippers [1] was not able to take into account the influence of the colloidal particles, Boerlage [4], after different tests, proposed a polyacrylonitrile membrane (PAN) with a MWCO of 13 kDa as a reference membrane for the determination of the MFI–UF. Using such a membrane, the cake filtration model may be applied, thus giving a physical meaning to the FI. The limiting parameter of the MFI–UF is the duration of the test (more than 20 h). Boerlage [5] later developed a method of determination at constant flux giving the value of MFI–UF in a shorter time (5 h).

*Corresponding author.

Presented at the International Congress on Membranes and Membrane Processes (ICOM), Seoul, Korea, 21–26 August 2005.

Roorda [6], using the same assumptions as Boerlage [4], defined Normalised MFI–UF. It was based on the same filtration equations as the ones used by Boerlage [4]. Roorda proposed to give the results under standard conditions [1 m^2 membrane area and 1 bar transmembrane pressure (TMP)]. Furthermore, specific tests have been proposed for assessing the membrane fouling rate when in operation. For instance, Rabie [7] defined the Normalized Fouling Rate that predicts the filtration period between two successive backwashes. The major advantage of this method is the optimization of long-term operation of a membrane unit using the analysis of initial performance.

Brauns et al. [8] proposed a quite similar approach by plotting the volume of permeate per membrane area vs. the loss of permeability of the membrane. They proved this method to be more accurate as for two kinds of water (tap and canal water) having the same value of MFI, but the graphs obtained were different. However, it can be considered that the FI should be used as an intrinsic character of water and not as a parameter for design purposes as it is evident that a standard test cannot be made under the same conditions as the full-scale operation.

Some time ago, Schippers [9] demonstrated that the value of MFI is MWCO dependent. Based on those results, including the more recent ones from Boerlage [2,4,5], it may be considered that the FI could be represented by the value of the specific resistance of the cake formed by the fouling components of the water deposited on a membrane during a standard filtration test. This was the original idea of Schippers [9] and he did it with UF membranes. However, when looking at the molecular weight (MW) (or molar mass) distribution of natural organic matter (NOM) and even more of effluent organic matter (EfOM), the existence of a fraction containing small molecules with low molecular weight [10,11] makes the use of a NF membrane more appropriate. It can be taken into account too that the analytical methods for the characterization of NOM and EfOM imply an initial step of separation using a dialysis membrane with a MWCO (or cut-off) of about 3500 Da (or g/mol); only the fraction not retained by this membrane is used for the fractionation process [12].

When considering the MW distribution of biologically treated secondary effluent, it is generally in the range of 0.5–50 kDa with a large fraction below 10 kDa[13]. These considerations are in favour of taking into account the solute fraction in the determination of the MFI.

The choice of membrane for the test is the result of a compromise between the desire to include all the potential fouling agents and the necessity of neglecting salt retention for having a simple interpretation of the result obtained. It has already been demonstrated that dead-end filtration of macromolecules obeys the conventional filtration equation [14]. Thus, a well-chosen NF membrane should be able to fulfill this task.

The purpose of our work was to use a NF membrane for the FI measurement with the hypothesis that a NF membrane is able to retain all the components responsible for fouling including small molecules (colloids and solutes) that are involved in membrane fouling. The cake formed contains all these components, and its specific resistance is supposed to be a good index of fouling phenomena. Using a NF membrane could result in salt and very small molecule retention, with the consequent build up of osmotic pressure. This is why a loose, uncharged NF membrane was chosen. This choice is discussed below.

2. Equipment and methods

2.1. Experimental device

The experiments were carried out in the laboratory-scale device described in Fig. 1. The flat-sheet NF membrane was installed in cell C. The characteristics of the NF membrane are summarized in Table 1.

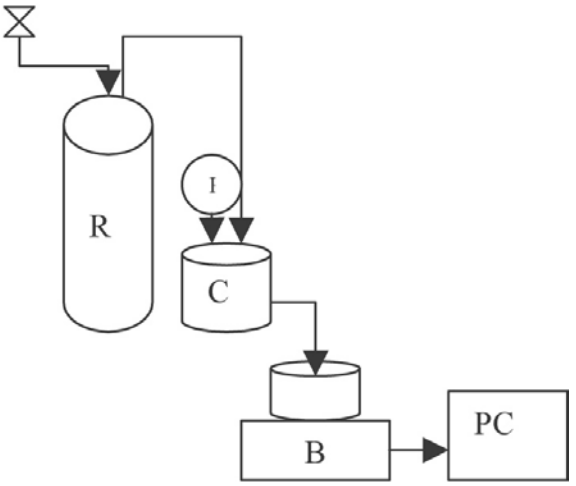

Fig. 1. Experimental set-up for the measurement of the NF–MFI.

Table 1
Characteristics of the NF membrane

Name	Permionics
Material	Hydrophylic polyether sulphone membranes with a thin-film oxidation resistant layer
MWCO (Dalton) [or cut-off (g/mol)]	1500; 500

Table 2
Characteristics of the UF membrane

Membrane	UF
Material	Polyether sulphone
MWCO, Dalton	30,000

The stirred reservoir (R) feeds the small cell. The pressure is maintained by compressed air and measured by a pressure gauge (P). The filtration is monitored in the dead-end mode. The permeate volume is recorded by a balance (B) which is connected to the computer (PC).

A UF membrane was used in order to compare the FI. The characteristics of this membrane are summarized in Table 2. Natural and synthetic EfOM solutions were used. The NOM solution was prepared by dilution Biohumic (Bioiberica). This product, composed of 85% humic and fulvic acids, is the result of an extraction from peat and has agricultural uses. The synthetic secondary treated sewage was prepared from persistent organic compounds that are slowly biodegradable [15]. The SUVA of both the NOM solution and synthetic secondary treated sewage are 80 and 30 $m^{-1}.mg^{-1}.L$, respectively. As the fouling of RO membranes used in desalination processes is a crucial issue, some samples of seawater were also tested.

2.3 Analytical methods

The influent and the effluent were analyzed by UV absorbance at 254 nm, which is the characteristic wavelength for humic substances. Conductivity and pH were monitored. The conductivity was monitored to ensure that there was no salt rejection during the experiments.

3. Results and discussion

3.1. Theoretical background

Making the hypothesis that the only mechanism that increases the apparent resistance during the filtration test is the formation of a cake on the membrane surface, the conventional equation of filtration at constant pressure may be used:

$$\frac{\partial V}{\partial t} = \frac{\Delta P}{\eta} \frac{A}{\left(R_m + R_c\right)} \tag{1}$$

After integration:

$$t = \frac{\eta V R_m}{\Delta P A} + \frac{\eta V^2 I}{2 \Delta P A^2} \tag{2}$$

$$t = \frac{\eta V R_m}{\Delta P A} + \frac{\eta V^2 \alpha W}{2\Delta P A^2} \quad (3)$$

and after simplification:

$$\frac{t}{V/A} = \frac{\eta R_m}{\Delta P} + \frac{\eta \alpha W}{2\Delta P}\frac{V}{A}$$
$$\frac{t}{V/A} = a + \mathrm{MFI} \times \frac{V}{A} \quad (4)$$

with

$$\mathrm{MFI} = \frac{\eta I}{2\Delta P} \quad (5)$$

Eqs. (4) and (5) are a definition of MFI where t is filtration time (s), V/A is the permeate volume produced per membrane area (m), ΔP the TMP (Pa), A the membrane area (m^2), R_m the resistance of the membrane (m^{-1}), R_c the resistance of the cake (m^{-1}); $I = \alpha W$ is the FI that is the product of the specific cake resistance (α) and concentration of particles (W) in the feed water (m^{-2}), and η is the dynamic viscosity of the water (N s.m^{-2}).

I was used rather than α due to a lack of analytical tools that could accurately determine the concentration of particles, colloids and macromolecules in feed water. $I = \alpha W$ has the dimension of the inverse of the permeability; thus, it can be considered as the " resistivity" of the cake.

3.2. Natural organic matter

The filtration of the NOM solution (initial TOC = 3.39 ppm) was performed at both 2 and 4 bar using a NF membrane (MWCO 1500Da). As can be seen in Fig. 2, the slopes are nearly similar, leading to a close value of MFI (Table 3). At first glance, this result may be considered as positive: MFI is the same for different conditions of filtration of the same sample. However, this is pure coincidence due to the compressibility of the cake formed with a compressibility factor of about one. In fact, due to this compressibility, the specific resistance of the formed cake is proportional to the pressure.

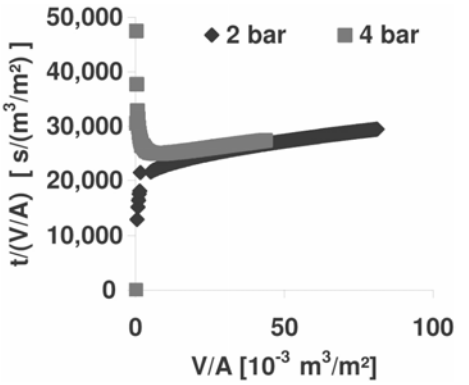

Fig. 2. Filtration of natural organic matter.

Table 3
Nanofiltration of NOM

	Pressure, bar	
	2	4
NF MFI (s/m^2)	70×10^3	72×10^3
Time required to get the beginning of the linearity (s)	1300	335
Correlation factor	0.9987	0.9996
R_m from the ordinate at the origin (m^{-1})	5.58×10^{12}	1.10×10^{13}
R_m from pure water flux (m^{-1})	5.23×10^{12}	8.76×10^{12}
Resistivity I (1/m²)	3.35×10^{13}	6.65×10^{13}

This membrane retained about 73% of the NOM. The conductivity had nearly the same values in the influent and permeate (96.4 and 98.7 µS/cm at 25°C for influent and permeate, respectively), confirming that the membrane has a low rejection of salts; thus, the TMP is the only driving force of the filtration.

From these initial experiments it was concluded that the dissolved organic matter is responsible for the fouling and has to be taken into account in the determination of the resis-

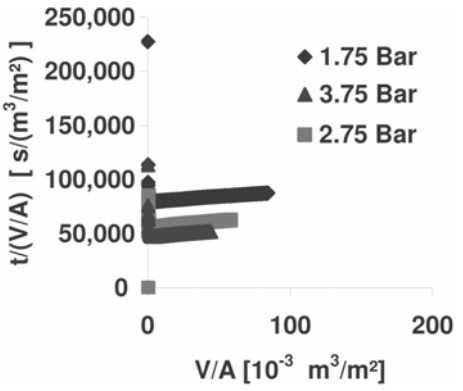

Fig. 3. Filtration of synthetic secondary treated sewage (initial TOC 4.90–5.42 ppm).

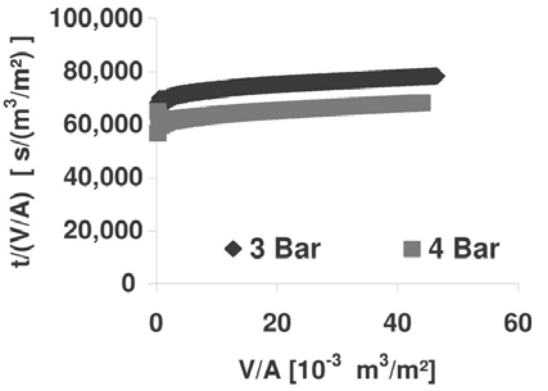

Fig. 4. Filtration of synthetic secondary treated sewage (initial TOC 10.10–10.97 ppm).

Table 4
Different parameters for the filtration of synthetic EfOM (initial TOC 4.90–5.42 ppm)

	Pressure, bar		
	1.75	2.75	3.75
NF MFI (s/m^2)	96×10^3	106×10^3	104×10^3
Time required to reach the onset of linearity (s)	375	1230	735
Correlation factor	0.9966	0.9991	0.9984
R_m from the ordinate at the origin (m^{-1})	1.61×10^{13}	1.76×10^{13}	2.02×10^{13}
R_m from pure water flux (m^{-1})	1.46×10^{13}	1.51×10^{13}	ND[a]
Resistivity I (1/m²)	3.87×10^{13}	6.63×10^{13}	8.83×10^{13}

Table 5
Parameters of filtration of synthetic EfOM (initial TOC 10.10–10.97 ppm)

	Pressure, bar	
	3	4
NF MFI (s/m^2)	115×10^3	115×10^3
Time required to get the onset of linearity (s)	1600	1500
Correlation factor	0.9978	0.9979
Rm from the ordinate at the origin (m^{-1})	2.58×10^{13}	3.03×10^{13}
Rm from pure water flux (m^{-1})	2.37×10^{13}	2.65×10^{13}
Resistivity I (1/m²)	8.18×10^{13}	1.10×10^{14}

tivity: this is why a membrane able to retain these solutes should be used.

3.2. Synthetic secondary treated sewage

The results of two series of experiments are presented that show the influence of the concentration of fouling matter and pressure. This synthetic secondary sewage contained solutes and suspended solids. NF membranes (MWCO 500 Da) were used in this study, with a new membrane for each test. The results are shown in Figs. 3 and 4 and Tables 4 and 5. According to Tables 4 and 5, the NF MFI was nearly the same regardless of the initial values of TOC and TMP. The increase of resistivity I with pressure was due to cake compressibility.

Despite its lower MWCO, the NF membrane chosen was still unable to retain all organic matter contained in the synthetic effluent The rejection was only 35–40%. This is probably due to the composition of this synthetic effluent, which contains an important fraction of

Table 6
Parameters of filtration of seawater

	NF	UF
Pressure (bar)	2	1
MFI (s/m^2)	99×10^3	99×10^3
Time required to get the beginning of the linearity (s)	1660	710
Correlation factor	0.9109	0.9987
R_m from the ordinate at the origin (m^{-1})	1.99×10^{13}	6.47×10^{11}
R_m from pure water flux (m^{-1})	1.66×10^{13}	5.79×10^{11}
Resistivity (1/m^2)	8.70×10^{12}	4.40×10^{12}

molecules which MW is below 0.5kDa. During this series of experiments, the conductivity of the water was not modified by filtration, confirming that the salts were not retained.

3.3. Fouling potential of seawater

Seawater (UV 254 nm = 0.90 cm^{-1}) was filtrated on two different membranes: UF and NF membranes of 500 Daltons (properties given in Tables 1 and 2). The results obtained are shown in Table 6 and Fig. 5.

MFI UF and MFI NF are similar in the case of the unique sample tested. This conclusion should be different depending on the characteristics of seawater (organic content). Although the MFI obtained by UF and NF were nearly similar, the resistivity was more important for NF than for UF; this is due to the difference in operating pressure for both experiments.

$\alpha W(I)$ should be taken as the representative parameter, with the advantage of having a physical meaning: the resistivity of the cake formed by the particles, colloids, and molecules retained by the membrane in standard conditions of dead-end filtration. In the case of compressible cakes (usually the case with organic matter), I is pressure dependent. This means that an operating pressure (for instance, 2 bars) has to be chosen when defining the conditions of a standard test.

4. Conclusions and outcome

This study showed that dissolved organics are responsible for fouling and have to be taken into account in determining the fouling potential of water. Using a loose NF or a NF membrane, the determination of a FI was possible in a short time (about 1 h).

Under standard conditions of operation, it was proposed to use product αW as the representative parameter of fouling ability. This parameter represents, in fact, the "resistivity" of a cake formed on NF membranes by all the components retained by the membrane and initially contained in the filtered volume.

Acknowledgments

The authors thank Polymem and Permionics for providing the membranes. They also thank Prof. Fane, Prof. Leslie and Dr. Guang for their help and for the use of equipment in their laboratory in the School of Chemical Engineering and Industrial Chemistry at The University of New South Wales; and Professor S. Vigneswaran and Doctor H.H. Ngo for allowing the use of analytical equipment in the Environmental Engineering R & D Laboratory of the University of Technology, Sydney.

The authors would like to thank the rewievers for their useful and valuable comments.

References

[1] J.C. Schippers and J. Verdouw, Desalination, 32 (1980) 137–148.
[2] S.F.E. Boerlage, M. Kennedy, M.P. Aniye and J.C. Schippers, JMS, 220 (2003) 97–116.
[3] J.S. Vrouwenvelder, J.W.N.M. Kappelhof, S.G.J.

Heijman, J.C. Schippers and D. van der Kooij, Desalination, 157 (2003) 361–365.
[4] S.F..E. Boerlage, M.D. Kennedy, M.R. Dickson, D.E.Y. El-Hodali and J.C. Schippers, JMS, 197 (2002) 1–21.
[5] S.F.E. Boerlage, M. Kennedy, Z. Tarawneh, R. De Faber and J.C. Schippers, Desalination, 161 (2004) 103–113.
[6] J.H. Roorda and J.H.J.M. Van der Graaf, Water Sci. Technol., 43 (2001) 241–248.
[7] H.R. Rabie, P. Côté and N. Adams, Desalination,141 (2001) 237–243.
[8] E. Brauns, E. Van Hoof, B. Molenberghs, C. Dotremont, W. Doyen and R. Leysen, Desalination, 150 (2002) 31–43.
[9] J.C. Schippers, J.H. Hanemaayer, C.A. Smolders and A. Kostense, Desalination, 38 (1981) 339–348.
[10] C. Jarusutthirak, G. Amy and J.-P. Croué, Desalination, 145 (2002) 247–255.
[11] D. Abdessemed, G. Nezzal and R. Ben Aim, Desalination, 146 (2002) 433–437.
[12] J.A. Leenheer, J.P. Croué, M. Benjamin, G.V. Korshin, C.J. Hwang, A. Brucher, G.R. and A. Aiken, ACS Symp. Series, 761 (2000) 68–83.
[13] D.J. Barker and D.C. Stuckey, Water Res., 33 (1999) 3063–3082.
[14] M. Shirato, T. Murase, E. Iritani and S. Nakatsuka, Fil. Sep., 28 (1991) 104–109.
[15] T. Seo, Y. Suzuki and S. Ohgaki, Desalination, 106 (1996) 39–45.